08/492,960

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶:

C22C 1/09, H01B 1/02

A1

(11) International Publication Number: WO 97/00976

(43) International Publication Date: 9 January 1997 (09.01.97)

US

(21) International Application Number: PCT/US96/07286

(22) International Filing Date: 21 May 1996 (21.05.96)

(30) Priority Data:

21 June 1995 (21.06.95)

(71) Applicant: MINNESOTA MINING AND MANUFACTUR-ING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

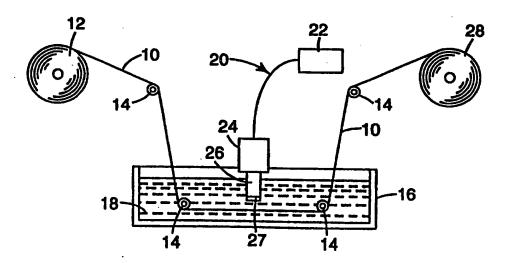
(72) Inventors: MCCULLOUGH, Colin; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MORTENSEN, Andreas; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WERNER, Paul, S.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). DEVE, Herve, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ANDERSON, Tracy, L.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: BERNSTEIN, David, B. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AU, CA, CN, JP, KR, NO, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

(54) Title: FIBER REINFORCED ALUMINUM MATRIX COMPOSITE



(57) Abstract

A composite metal matrix formed of polycrystalline α -Al₂O₃ fibers encapsulated within a matrix of substantially pure elemental aluminum, or an alloy elemental aluminum and up to about 2 % copper is disclosed. The resulting materials are characterized by their high strength and low weight are particularly well suited for applications in various industries including high voltage power transmission.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	TE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	
CH	Switzerland	KZ	Kazakhstan	SI	Singapore Slovenia
CI	Côte d'Ivoire	L	Liechtenstein	SK	
CM	Cameroon	LK	Sri Lanka	SN	Slovakia
CN	China	LR	Liberia	SZ	Senegal
CS	Czechoslovakia	LT	Lithuania	SZ TD	Swaziland
CZ	Czech Republic	LU	Luxemboure		Chad
DE	Germany	LV	Latvia	TG	Togo
DK	Denmark	MC	Monaco	TJ TT	Tajikistan
EE	Estonia	MD	Republic of Moldova		Trinidad and Tobago
ES	Spain	MG	Madagascar	UA	Ukraine
FI	Finland	ML	Mali	UG	Uganda
FR	Prance	MN	Mongolia	US	United States of America
GA	Gabon	MR	Mauritania	UZ	Uzbekistan
		1411	AND THE LINE AND THE PERSON NAMED IN COLUMN TWO IN COLUMN	VN	Viet Nam

FIBER REINFORCED ALUMINUM MATRIX COMPOSITE

Government License Rights

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of contract No. MDA 972-90-C-0018 awarded by the Defense Advanced Research Projects Agency (DARPA).

Field of the Invention

10

5

The present invention pertains to composite materials of ceramic fibers within in an aluminum matrix. Such materials are well-suited for various applications in which high strength, low weight materials are required.

Background of the Invention

15

20

25

30

Continuous fiber reinforced aluminum matrix composites (CF-AMCs) offer exceptional specific properties when compared to conventional alloys and to particulate metal matrix composites. The longitudinal stiffness of such composite materials is typically three times that of conventional alloys, and the specific strength of such composites is typically twice that of high-strength steel or aluminum alloys. Furthermore, for many applications, CF-AMCs are particularly attractive when compared to graphite-polymer composites due to their more moderate anisotropy in properties, particularly their high strength in directions different that those of the fiber axes. Additionally, CF-AMCs offer substantial improvements in allowable service temperature ranges and do not suffer from environmental problems typically encountered by polymeric matrix composites. Such problems include delamination and degradation in hot and humid environments, particularly when exposed to ultraviolet (UV) radiation.

Despite their numerous advantages, known CF-AMCs suffer drawbacks which have hampered their use in many engineering applications. CF-AMCs generally feature high modulus or high strength, but seldom combine both properties. This feature is taught in Table V of R.B. Bhagat, "Casting Fiber-

Reinforced Metal Matrix Composites", in Metal Matrix Composites: Processing and Interfaces, R.K. Everett and R.J. Arsenault Eds., Academic Press, 1991, pp. 43-82. In that reference, properties listed for cast CF-AMC only combine a strength in excess of 1 GPa with a modulus in excess of 160 GPa in high-strength carbon-reinforced aluminum, a composite which suffers from low transverse strength, low compressive strength, and poor corrosion resistance. At the present time, the most satisfactory approach for producing CF-AMCs in which high strength in all directions is combined with a high modulus in all directions is with fibers produced by chemical vapor deposition. The resulting fibers, typically boron, are very expensive, too large to be wound into preforms having a small-radius of curvature, and chemically reactive in molten aluminum. Each of these factors significantly reduces the processability and commercial desirability of the fiber.

5

10

15

20

25

30

Furthermore, composites such as aluminum oxide (alumina) fibers in aluminum alloy matrices suffer from additional drawbacks during their manufacture. In particular, during the production of such composite materials, it has been found to be difficult to cause the matrix material to completely infiltrate fiber bundles. Also, many composite metal materials known in the art suffer from insufficient long-term stability as a result of chemical interactions which can take place between the fibers and the surrounding matrix, resulting in fiber degradation over time. In still other instances, it has been found to be difficult to cause the matrix metal to completely wet the fibers. Although attempts have been made to overcome these problems (notably, providing the fibers with chemical coatings to increase wetability and limit chemical degradation, and using pressure differentials to assist matrix infiltration) such attempts have met with only limited success. For example, the resulting matrices have, in some instances, been shown to have decreased physical characteristics. Furthermore, fiber coating methods typically require the addition of several complicated process steps during the manufacturing process.

In view of the above, a need exists for ceramic fiber metal composite materials that offer improved strength and weight characteristics, are free of long term degradation, and which may be produced using a minimum of process steps.

Summary of the Invention

The present invention relates to continuous fiber aluminum matrix composites having wide industrial applicability. In its broadest form, the invention pertains to continuous fiber aluminum matrix composites characterized by the use of continuous high-strength, high-stiffness fibers that are contained within a matrix material that is free of contaminants likely to cause brittle intermetallic compounds or phases, or segregated domains of contaminant material at the matrix/fiber interface. The matrix material is selected to have a relatively low yield strength whereas the fibers are selected to have a relatively high tensile strength. Furthermore, the materials are selected such that the fibers are relatively chemically

inert in the matrix in both its molten and solid phases.

More particularly, the present invention relates to composite materials having continuous fibers of polycrystalline α -Al₂O₃ (tensile strength about 2.8 GPa) contained within a matrix of elemental aluminum (yield strength about 20 MPa) or an alloy of elemental aluminum containing up to about 2% copper (yield strength about 80 MPa). Such composite structures have been shown to offer high strength and low weight, while at the same time avoiding the potential for long term degradation. Such composites may also be made without the need for many of the process steps associated with prior art composite materials.

20

25

5

10

15

In one embodiment, the continuous fiber aluminum matrix composites of the present invention can be formed into wires exhibiting desirable strength-to-weight characteristics and high electrical conductivity. Such wires are well-suited for use as core materials in high voltage power transmission (HVPT) cables, as they provide electrical and physical characteristics which offer improvements over HVPT cables known in the prior art.

Brief Description of the Drawings

FIG. 1 is a schematic representation of an apparatus for producing composite metal matrix wires using ultrasonic energy.

30

FIGS. 2a and 2b are schematic, cross-sections of two embodiments of overhead high voltage transmission cables having composite metal matrix cores.

FIG. 3 is a chart comparing strength-to-weight ratios for materials of the present invention with other materials.

FIGS. 4a and 4b are graphs comparing projected sag as a function of span length for various cables.

FIG. 5 is a graph showing the coefficient of thermal expansion as a function of temperature for a CF-AMC wire.

5

10

15

20

25

30

Detailed Description

The fiber reinforced aluminum matrix composites of the present invention comprise continuous fibers of polycrystalline α -Al₂O₃ encapsulated within either a matrix of substantially pure elemental aluminum or an alloy of pure aluminum with up to about 2% copper by weight. The preferred fibers have an equiaxed grain size of less than about 100 nm, and a fiber diameter in the range of about 1-50 micrometers. A fiber diameter in the range of about 5-25 micrometers is preferred with a range of about 5-15 micrometers being most preferred. Preferred composite materials have a fiber density of between about 3.90-3.95 grams per cubic centimeter. Among the preferred fibers are those described in U.S. Patent No. 4,954,462 (Wood et al., assigned to Minnesota Mining and Manufacturing Company, St. Paul, MN) the teachings of which are hereby incorporated by reference. Such fibers are available commercially under the designation NEXTEL™ 610 ceramic fibers from the Minnesota Mining and Manufacturing Company, St. Paul, MN. The encapsulating matrix is selected to be such that it does not react chemically with the fiber material, thereby eliminating the need to provide a protective coating on the fiber exterior.

As used herein, the term "polycrystalline" means a material having predominantly a plurality of crystalline grains in which the grain size is less than the diameter of the fiber in which the grains are present. The term "continuous" is intended to mean a fiber having a length which is relatively infinite when compared to the fiber diameter. In practical terms, such fibers have a length on the order of about 15 cm to at least several meters, and may even have lengths on the order of kilometers or more.

- 4 -

In the preferred embodiments, the use of a matrix comprising either substantially pure elemental aluminum, or an alloy of elemental aluminum with up to about 2% copper has been shown to produce successful composites. As used herein the terms "substantially pure elemental aluminum", "pure aluminum" and "elemental aluminum" are interchangeable and are intended to mean aluminum containing less than about 0.05% impurities by weight. Such impurities typically comprise first row transition metals (titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and zinc) as well as second and third row metals and elements in the lanthanide series. In one preferred embodiment, the terms are intended to mean aluminum having less than about 0.03% iron by weight, with less than about 0.01% iron by weight being most preferred. Minimizing the iron content is desirable because iron is a common contaminant of aluminum, and further, because iron and aluminum combine to form brittle intermetallic compounds (e.g., Al₃Fe, Al₂Fe, etc.). It is also particularly desirable to avoid contamination by silicon (such as from SiO2, which can be reduced to free silicon in the presence of molten aluminum) because silicon, like iron, forms a brittle phase, and because silicon can react with the aluminum (and any iron which may be present) to form brittle Al-Fe-Si intermetallic compounds. The presence of brittle phases in the composite is undesirable, as such phases tend to promote fracture in the composite when subjected to stress. In particular, such brittle phases may cause the matrix to fracture even before the reinforcing ceramic fibers fracture, resulting in composite failure. Generally, it is desirable to avoid substantial amounts of any transition metal, (i.e., Groups IB through VIIIB of the periodic table), that form brittle intermetallic compounds. Iron and silicon have been particularly specified herein as a result of their commonality as impurities in metallurgical processes.

25

5

10

15

20

Each of the first row transition metals described above is relatively soluble in molten aluminum and, as noted, can react with the aluminum to form brittle intermetallic compounds. In contrast, metal impurities such as tin, lead, bismuth, antimony and the like do not form compounds with aluminum, and are virtually insoluble in molten aluminum. As a result, those impurities tend to segregate to the fiber/matrix interface, thereby weakening the composite strength at the interface. Although such segregation may aid longitudinal strength of the

ultimate composite by contributing to a global load sharing domain (discussed below), the presence of the impurities ultimately results in a substantial reduction in the transverse strength of the composite due to decohesion at the fiber/matrix interface. Elements from Groups IA and IIA of the periodic table tend to react with the fiber and drastically decrease the strength of the fiber in the composite. Magnesium and lithium are particularly undesirable elements in this regard, due, in part, to the length of time the fibers and the metal must be maintained at high temperatures during processing or in use.

5

10

15

20

25

30

It should be understood that references to "substantially pure elemental aluminum", "pure aluminum", and "elemental aluminum" as used herein, are intended to apply to the matrix material rather than to the reinforcing fibers, since the fibers will likely include domains of iron (and possibly other) compounds within their grain structure. Such domains typically are remnants of the fiber manufacturing process and have, at most, negligible effect on the overall characteristics of the resulting composite material, since they tend to be relatively small and fully encapsulated within the grains of the fiber. As such, they do not interact with the composite matrix, and thereby avoid the drawbacks associated with matrix contamination.

The metal matrix used in the composite of the present invention is selected to have a low yield strength relative to the reinforcing fibers. In this context, yield strength is defined as the stress at 0.2% offset strain in a standardized tensile test of the unreinforced metal or alloy. Generally, two classes of aluminum matrix composites can be broadly distinguished based on the matrix yield strength. Composites in which the matrix has a relatively low yield strength have a high long tudinal tensile strength governed primarily by the strength of the reinforcing fibers. As used herein, low yield strength aluminum matrices in aluminum matrix composites are defined as matrices with a yield strength of less than about 150 MPa. The matrix yield strength is preferably measured on a sample of matrix material having the same composition and which has been fabricated in the same manner as the material used to form the composite matrix. Thus, for example, the yield strength of a substantially pure elemental aluminum matrix material used in a

composite material would be determined by testing the yield strength of substantially pure elemental aluminum without a fiber reinforcement. The test method preferably follows the ASTM tensile test standard E345-93 (Standard Test Methods of Tension Testing of Metallic Foil). In composites with low yield-strength matrices, matrix shearing in the vicinity of the matrix-fiber interface reduces the stress concentrations near broken fibers and allows for global stress redistribution. In this regime, the composite reaches "rule-of-mixtures" strength. Pure aluminum has a yield strength of less than about 13.8 MPa (2 ksi) and Al-2 wt% Cu has a yield strength less than about 96.5 MPa (14 ksi).

10

15

5

The low yield-strength matrix composites described above may be contrasted with high yield strength matrices which typically exhibit lower composite longitudinal strength than the predicted "rule-of-mixtures" strength. In composites having high strength matrices, the characteristic failure mode is a catastrophic crack propagation. In composite materials, high yield strength matrices typically resist shearing from broken fibers, thereby producing a high stress concentration near any fiber breaks. The high stress concentration allows cracks to propagate, leading to failure of the nearest fiber and catastrophic failure of the composite well before the "rule-of-mixtures" strength is reached. Failure modes in this regime are said to result from "local load sharing". For a metal matrix composite with about 50 volume percent fiber, a low yield strength matrix produces a strong (i.e., > 1.17 GPa (170 ksi)) composite when combined with alumina fibers having strengths of greater than 2.8 GPa (400 ksi). Thus, it is believed that for the same fiber loading, the composite strength will increase with fiber strength.

25

20

The strength of the composite may be further improved by infiltrating the polycrystalline α-Al₂O₃ fiber tows with small domains, in the form of particles, whiskers or short (chopped) fibers, of alumina. Such domains, typically on the order of less than 20 micrometers, and often submicron, become physically trapped at the fiber surface and provide for spacing between individual fibers within the composite. The spacing eliminates interfiber contact and thereby yields a stronger composite. A discussion of the use of small domains of material to minimize interfiber contact can be found in U.S. Patent No. 4,961,990 (Yamada et

al., assigned to Kabushiki Kaisha Toyota Chuo Kenkyusho and Ube Industries, Ltd., both of Japan).

As noted above, one of the significant obstacles in forming composite materials relates to the difficulty in sufficiently wetting reinforcing fibers with the surrounding matrix material. Likewise, infiltration of the fiber tows with the matrix material is also a significant problem in the production of composite metal matrix wires, since the continuous wiring forming process typically takes place at or near atmospheric pressure. This problem also exists for composite materials formed in batch processes at or near atmospheric pressure.

10

15

5

The problem of incomplete matrix infiltration of the fiber tow can be overcome through the use of a source of ultrasonic energy as a matrix infiltration aid. For example, U.S. Patent No. 4,779,563 (Ishikawa et al., assigned to Agency of Industrial Science and Technology, Tokyo, Japan), describes the use of ultrasonic wave vibration apparatus for use in the production of preform wires, sheets, or tapes from silicon carbide fiber reinforced metal composites. The ultrasonic wave energy is provided to the fibers via a vibrator having a transducer and an ultrasonic "horn" immersed in the molten matrix material in the vicinity of the fibers. The horn is preferably fabricated of a material having little, if any, solubility in the molten matrix to thereby prevent the introduction of contaminants into the matrix. In the present case, horns of commercially pure niobium, or alloys of 95% niobium and 5% molybdenum have been found to yield satisfactory results. The transducer used therewith typically comprises titanium.

20

25

One embodiment of a metal matrix fabrication system employing an ultrasonic horn is presented in FIG. 1. In that Figure, a polycrystalline α -Al₂O₃ fiber tow 10 is unwound from a supply roll 12 and drawn, by rollers 14, through a vessel 16 containing the matrix metal 18 in molten form. While immersed in the molten matrix metal 18, the fiber tow 10 is subjected to ultrasonic energy provided by an ultrasonic energy source 20 which is immersed in the molten matrix metal 18 in the vicinity of a section of the tow 10. The ultrasonic energy source 20 comprises an oscillator 22 and a vibrator 24 having a transducer 26 and a horn 27. The horn 27 vibrates the molten matrix metal 18 at a frequency produced by the

5

10

15

20

25

30

oscillator 22 and transmitted to the vibrator 24 and transducer 26. In so doing, the matrix material is caused to thoroughly infiltrate the fiber tow. The infiltrated tow is drawn from the molten matrix and stored on a take-up roll 28.

The process of making a metal matrix composite often involves forming fibers into a "preform". Typically, fibers are wound into arrays and stacked. Fine diameter alumina fibers are wound so that fibers in a tow stay parallel to one another. The stacking is done in any fashion to obtain a desired fiber density in the final composite. Fibers can be made into simple preforms by winding around a rectangular drum, a wheel or a hoop. Alternatively, they can be wrapped onto a cylinder. The multiple layers of fibers wound or wrapped in this fashion are cut off and stacked or bundled together to form a desired shape. Handling the fiber arrays is aided by using water either straight or mixed with an organic binder to hold the fibers together in a mat.

One method of making a composite part is to position the fibers in a mold, filling the mold with molten metal, and then subjecting the filled mold to elevated pressure. Such a process is disclosed in U.S. Patent No. 3,547,180 entitled "Production of Reinforced Composites". The mold should not be a source of contamination to the matrix metal. In one embodiment, the molds can be formed of graphite, alumina, or alumina-coated steel. The fibers can be stacked in the mold in a desired configuration; e.g., parallel to the walls of the mold, or in layers arrayed perpendicular to one another, as is known in the art. The shape of the composite material can be any shape into which a mold can be made. As such, fiber structures can be fabricated using numerous preforms, including, but not limited to, rectangular drums, wheel or hoop shapes, cylindrical shapes, or various molded shapes resulting from stacking or otherwise loading fibers in a mold cavity. Each of the preforms described above relates to a batch process for making a composite device. Continuous processes for the formation of substantially continuous wires, tapes, cables and the like may be employed as well. Typically, only minor machining of the surface of a finished part is necessary. It is possible also to machine any shape from a block of the composite material by using diamond tooling. Thus, it becomes possible to produce many complex shapes.

A wire shape can be formed by infiltrating bundles or tows of alumina fiber with molten aluminum. This can be done by feeding tows of fibers into a bath of molten aluminum. To obtain wetting of the fibers, an ultrasonic horn is used to agitate the bath while the fibers pass through it.

5

Fiber reinforced metal matrix composites are important for applications wherein lightweight, strong, high-temperature-resistant (at least about 300°C) materials are needed. For example, the composites can be used for gas turbine compressor blades in jet engines, structural tubes, actuator rods, I-beams, automotive connecting rods, missile fins, fly wheel rotors, sports equipment (e.g., golf clubs) and power transmission cable support cores. Metal matrix composites are superior to unreinforced metals in stiffness, strength, fatigue resistance, and wear characteristics.

10

In one preferred embodiment of the present invention, the composite material comprises between about 30-70% polycrystalline α -Al₂O₃ fibers within a substantially elemental aluminum matrix. It is preferred that the matrix contains less than about 0.03% iron, and most preferably less than about 0.01% iron. A fiber content of between about 40-60% polycrystalline α -Al₂O₃ fibers by weight is preferred. Such composites, formed with a matrix having a yield strength of less than about 20 MPa and fibers having a longitudinal tensile strength of at least about 2.8 GPa have been found to have excellent strength characteristics.

20

25

15

As noted above, the matrix may also be formed from an alloy of elemental aluminum with up to about 2% copper by weight. As in the embodiment in which a substantially pure elemental aluminum matrix is used, composites having an aluminum/copper alloy matrix preferably comprise between 30-70% polycrystalline α -Al₂O₃ fibers by weight, and more preferably 40-60% polycrystalline α -Al₂O₃ fibers by weight. In addition, as above, the matrix preferably contains less than about 0.03% iron, and most preferably less than about 0.01% iron. The aluminum/copper matrix preferably has a yield strength of less than about 80 MPa, and, as above, the polycrystalline α -Al₂O₃ fibers have a longitudinal tensile strength of at least about 2.8 GPa. The properties of two composites, a first with an elemental aluminum matrix, and a second with a matrix

of the specified aluminum/copper alloy, each having between about 55-65 vol. % polycrystalline α -Al₂O₃ fibers are presented in Table I below:

Table I: SUMMARY OF COMPOSITE PROPERTIES (1)

	or court opili	2 1 KOI EKTIES
	Pure Al 55-65 vol% Al ₂ O ₃	Al-2wt%Cu 55-65 vol% Al ₂ O ₃
Longitudinal Young's Modulus, E ₁₁ ⁽²⁾	220 - 260 GPa (32 - 38 Msi)	220 - 260 GPa (32 - 38 Msi)
Transverse Young's Modulus, E ₂₂	120 - 140 GPa (17.5 - 20 Msi)	150 - 160 GPa (22 - 23 Msi)
Shear Modulus, G ₁₂	48 - 50 GPa (6.5 - 7.3 Msi)	45 - 47 GPa (6.5 - 6.8 Msi)
Shear Modulus, G ₂₁	54 - 57 GPa (7.8 - 8.3 Msi)	55 - 56 GPa (8 - 8.2 Msi)
Long. tensile strength S ₁₁ , _T	1500 - 1900 MPa (220 - 275 ksi)	1500 - 1800 MPa (220 - 260 ksi)
Long. compressive strength, S ₁₁ , _C	1700 - 1800 MPa (245 - 260 ksi)	3500 - 3700 MPa (500 - 540 ksi)
Shear Strength S ₂₁ - S ₁₂ at 2% strain	70 MPa (10 ksi)	140 MPa (20 ksi)
Trans. strength S ₂₂ at 1% strain	110 - 130 MPa (16 - 19 ksi)	270 - 320 MPa (39 - 46 ksi)
(1)	1	į.

The properties listed in this table represent a range of mechanical performance measured on composites containing 55-65 vol% NEXTELTM 610 ceramic fibers. The range is not representative of the statistical scatter.

⁽²⁾ Index Notation

^{1 =} Fiber direction; 2 = Transverse direction; ij:i direction normal to the plane in which the stress is acting, j = stress direction, S = Ultimate strength unless specified.

Although suitable for a wide variety of uses, in one embodiment, the composites of the present invention have applicability in the formation of composite matrix wire. Such wires are formed from substantially continuous polycrystalline α -Al₂O₃ fibers contained within the substantially pure elemental aluminum matrix or the matrix formed from the alloy of elemental aluminum and up to about 2% copper described above. Such wires are made by a process in which a spool of substantially continuous polycrystalline α -Al₂O₃ fibers, arranged in a fiber tow, is provided. The fiber tow is pulled through a bath of molten matrix material. The resulting segment is then solidified, thereby providing fibers encapsulated within the matrix. It is preferred that an ultrasonic horn, as described above, is lowered into the molten matrix bath and used to aid the infiltration of the matrix into the fiber tows.

5

10

15

20

25

30

Composite metal matrix wires, such as those described above, are useful in numerous applications. Such wires are believed to be particularly desirable for use in overhead high voltage power transmission cables due to their combination of low weight, high strength, good electrical conductivity, low coefficient of thermal expansion, high use temperatures, and resistance to corrosion. The competitiveness of composite metal matrix wires, such as those described above for use in overhead high voltage power transmission, is a result of the significant effect cable performance has on the entire electricity transport system. Cable having lower weight per unit strength, coupled with increased conductivity and lower thermal expansion, provides the ability to install greater cable spans and/or lower tower heights. As a result, the costs of constructing electrical towers for a given electricity transport system can be significantly reduced. Additionally, improvements in the electrical properties of a conductor can reduce electrical losses in the transmission system, thereby reducing the need for additional power generation to compensate for such losses.

As noted above, the composite metal matrix wires of the present invention are believed to be particularly well-suited for use in overhead high voltage power transmission cables. In one embodiment, an overhead high voltage power transmission cable can include a conductive core formed by at least one composite

metal matrix wire. The core is surrounded by at least one conductive jacket formed by a plurality of aluminum or aluminum alloy wires. Numerous cable core and jacket configurations are known in the cable art. For example, as shown in FIG. 2a, the cross-section of one overhead high voltage power transmission cable 30 may be a core 32 of nineteen individual composite metal matrix wires 34 surrounded by a jacket 36 of thirty individual aluminum or aluminum alloy wires 38. Likewise, as shown in FIG. 2b, as one of many alternatives, the cross section of a different overhead high voltage power transmission cable 30' may be a core 32' of thirty-seven individual composite metal matrix wires 34' surrounded by a jacket 36' of twenty-one individual aluminum or aluminum alloy wires 38'.

5

10

15

20

25

30

The weight percentage of composite metal matrix wires within the cable will depend upon the design of the transmission line. In that cable, the aluminum or aluminum alloy wires used in the conductive jackets are any of the various materials known in the art of overhead high voltage power transmission, including, but not limited to, 1350 Al or 6201 Al.

In another embodiment, an overhead high voltage power transmission cable can be constructed entirely of a plurality of continuous fiber aluminum matrix composite wires (CF-AMCs). As is discussed below, such a construction is well-suited for long cable spans in which the strength-to-weight ratio and the coefficient of thermal expansion of the cable overrides the need to minimize resistive losses.

Although dependent upon a number of factors, the amount of sag in an overhead high voltage power transmission cable varies as the square of the span length and inversely with the tensile strength of the cable. As may be seen in FIG. 3, CF-AMC materials offer substantial improvements in the strength-to-weight ratio over materials commonly used for cable in the power transmission industry. It should be noted that the strength, conductivity and density of CF-AMC materials and cables is dependent upon the fiber volume in the composite. For FIGS. 3, 4a, 4b, and 5 a 50% fiber volume was assumed, with a corresponding density of about 3.2 gm/cm³ (approximately 0.115 lb/in³), tensile strength of 1.38 GPa (200 ksi), and conductivity of 30% IACS.

As a result of the increased strength of cables containing CF-AMC wires, cable sag can be substantially reduced. Calculations comparing the sags of CF-AMC cables as a function of span length with a commonly used steel stranding (ACSR) (31 wt% steel having a core of 7 steel wires surrounded by a jacket of 26 aluminum wires), and an equivalent all-aluminum alloy conductor (AAAC) are shown in FIGS. 4a and 4b. All cables had equivalent conductivity and diameter. FIG. 4a demonstrates that CF-AMC cables provide for a 40% reduction in tower height as compared to ACSR for spans of about 550 m (about 1800 ft). Likewise, CF-AMC cables allow for an increase in span length about 25% assuming allowable sags of 15 m (about 50 ft). Further advantages from the use of CF-AMC cables in long spans are presented in FIG. 4b. In FIG. 4b, the ACSR cable was 72 wt% steel having a core of 19 steel wires surrounded by a jacket of 16 aluminum wires).

5

10

. 15

20

25

30

The sag of a high voltage power transmission (HVPT) cable at its maximum operating temperature is also dependent upon the coefficient of thermal expansion (CTE) of the cable at its maximum operating temperature. The ultimate CTE of the cable is determined by the CTE and the elastic modulus of both the reinforcing core and the surrounding strands. Within limits, materials with a low CTE and a high elastic modulus are desired. The CTE for the CF-AMC cable is shown in FIG. 5 as a function of temperature. Reference values for aluminum and steel are provided as well.

It is noted that the present invention is not intended to be limited to wires and HVPT cables employing composite metal matrix technology; rather, it is intended to include the specific inventive composite materials described herein as well as numerous additional applications. Thus, the composite metal matrix materials described herein may be used in any of a wide variety of applications, including, but not limited to, flywheel rotors, high performance aerospace components, voltage transmission, or many other applications in which high strength, low density materials are desired.

It should be further noted that although the preferred embodiment makes use of the polycrystalline α -Al₂O₃ fibers described in U.S. Patent No. 4,954,462 (previously incorporated) currently being marketed under the tradename

NEXTELTM 610 by Minnesota Mining and Manufacturing Company of St. Paul, MN, the invention is not intended to be limited to those specific fibers. Rather, any polycrystalline α-Al₂O₃ fiber is intended to be included herein as well. It is preferred, however, that any such fiber have a tensile strength at least on the order of that of the NEXTELTM 610 fibers (approximately 2.8 GPa).

In the practice of the invention, the matrix must be chemically inert relative to the fiber over a temperature range between about 20°C- 760°C. The temperature range represents the range of predicted processing and service temperatures for the composite. This requirement minimizes chemical reactions between the matrix and fiber which may be deleterious to the overall composite properties. In the case of a matrix material comprising an alloy of elemental aluminum and up to about 2% copper, the as-cast alloy has a yield strength of approximately 41.4-55.2 MPa (6-8 ksi). In order to increase the strength of this metal alloy, various treatment methods may be used. In one preferred embodiment, once combined with the metallic fibers, the alloy is heated to about 520°C for about 16 hours followed by quenching in water maintained at a temperature of between about 60-100°C. The composite is then placed in an oven and maintained at about 190°C and maintained at that temperature until the desired strength of the matrix is achieved (typically 0-10 days). The matrix has been found to reach a maximum yield strength of about 68.9-89.6 MPa (10-13 ksi) when it was maintained at a temperature of approximately 190°C for five days. In contrast, pure aluminum that is not specifically heat treated has a yield strength of approximately 6.9-13.8 MPa (1-2 ksi) in the as-cast state.

25

5

10

15

20

Examples

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

Test Methods

Fiber strength was measured using a tensile tester (commercially available as Instron 4201 tester from Instron of Canton, MA). This test is described in ASTM D 3379-75, (Standard Test Methods for Tensile Strength and Young's Modulus for High Modulus Single-Filament Materials). The specimen gauge length was 25.4 mm (1 inch), the strain rate was 0.02 mm/mm/min.

To establish the tensile strength of a fiber tow, ten single fiber filaments were randomly chosen from a tow of fibers. Each filament was tested to determine its breaking load. At least 10 filaments were tested with the average strength of the filaments in the tow being determined. Each individual, randomly selected fiber had strength ranging from 2.06 - 4.82 GPa (300 -700 ksi). The average individual filament tensile strength ranged from 2.76 to 3.58 GPa (400-520 ksi).

Fiber diameter was measured optically using an attachment to an optical microscope (Dolan-Jenner Measure-Rite Video Micrometer System, Model M25-0002, commercially available from Dolan-Jenner Industries, Inc. of Lawrence MA) at x1000 magnification. The apparatus used reflected light observation with a calibrated stage micrometer.

The breaking stress of each individual filament was calculated as the load per unit area.

The fiber elongation was determined from the load displacement curve and ranged from about 0.55% to about 1.3%.

For the practice of this invention, the average fiber strength was greater than 2.76 GPa (400 ksi) (with 15% standard deviation typical). The higher the average strength of the reinforcing fiber, the higher the composite strength. Composites made according to this invention had a strength of at least 1.38 GPa (200 ksi) (with 5% standard deviation), and often at least 1.72 GPa (250 ksi) (with 5% standard deviation) when provided with a fiber volume fraction of approximately 60%.

Tensile Testing

5

10

15

20

25

30

The tensile strength of the composite was measured using a tensile tester (commercially available as an Instron 8562 Tester from Instron Corp. of Canton, MA).

This test is carried out substantially as described for the tensile testing of metal foils, i.e., as described in ASTM E345-93, (Standard Test Methods for Tension Testing of Metallic Foil).

In order to perform tensile testing, the composite was made into a plate $15.24 \text{ cm} \times 7.62 \text{ cm} \times 0.13 \text{ cm} (6"x 3"x 0.05")$. Using a diamond saw, this plate was cut into 7 coupons ($15.24 \text{ cm} \times 0.95 \text{ cm} \times 0.13 \text{ cm} (6" \times 0.375" \times 0.05")$) which were used for testing.

Average longitudinal strength (i.e., fiber parallel to test direction) was measured at 1.38 GPa (200 ksi) for composites having a matrix of either pure aluminum or aluminum with 2% Cu. For composites having a fiber volume content of about 60%, average transverse strength (i.e., fiber perpendicular to the test direction) was 138 MPa (20 ksi) for composites containing pure aluminum and 262 MPa (38 ksi) for composites made with the aluminum/2% copper alloy.

Specific examples of various composite metal matrix fabrications are described below.

Example 1 - Preparation of a fiber-reinforced metal composite

5

10

15

20

25

30

A composite was prepared using an alumina fiber tow of NEXTELTM 610 ceramic fibers. The tow contained 420 fibers. The fibers were substantially round in cross-section and had diameters ranging from approximately 11-13 micrometers on average. The average tensile strength of the fibers (measured as described above) ranged from 2.76 - 3.58 GPa (400 - 520 ksi). Individual fibers had strengths ranging from 2.06 - 4.82 GPa (300 - 700 ksi).

The fibers were prepared for infiltration with metal by winding the fibers into a "preform". In particular, the fibers were wet with distilled water and vound around a rectangular drum having a circumference of approximately 86.4 cm (34 inches) in multiple layers to the desired preform thickness of approximately 0.25 cm (0.10 in).

The wound fibers were cut from the drum and stacked in the mold cavity to produce the final desired preform thickness. A graphite mold in the shape of a rectangular plate was used. Approximately 1300 grams of aluminum metal

5

10

15

20

25

30

(commercially available as Grade 99.99% from Belmont Metals of Brooklyn, NY) were placed into the casting vessel.

The mold containing the fibers was placed into a pressure infiltration casting apparatus. In this apparatus, the mold was placed into an airtight vessel or crucible and positioned at the bottom of an evacuable chamber. Pieces of aluminum metal were loaded into the chamber on a support plate above the mold. Small holes (approximately 2.54 mm in diameter) were present in the support plate to permit passage of molten aluminum to the mold below. The chamber was closed and the chamber pressure was reduced to 3 milliTorr to evacuate the air from the mold and the chamber. The aluminum metal was heated to 720°C and the mold (and fibrous preform in it) was heated to at least about 670°C. The aluminum melted at this temperature but remained on the plate above the mold. In order to fill the mold, the power to the heaters was turned off, and the chamber was pressurized by filling with argon to a pressure of 8.96 MPa (1300 psi). The molten aluminum immediately flowed through the holes in the support plate and into the mold. The temperature was allowed to drop to 600°C before venting the chamber to the atmosphere. After the chamber had cooled to room temperature, the part was removed from the mold. The resulting samples had dimensions of 15.2 cm x 7.6 cm x 0.13 cm (6" x 3" x 0.05").

The sample rectangular composite pieces contained 60 volume % fiber. The volume fraction was measured by using the Archimedes principle of fluid displacement and by examining a photomicrograph of a polished cross-section at 200x magnification.

The part was cut into coupons for tensile testing, it was not machined further. The tensile strength, measured from coupons as described above, was 1400 MPa (204 ksi)(longitudinal strength) and 140 MPa (20.4 ksi) (transverse strength).

Example 2-Preparation of Metal Matrix Composite Wires

The fibers and metal used in this example were the same as those described in Example 1. The alumina fiber was not made into a preform. Instead, the fibers (in the form of multiple tows) were fed into a molten bath of aluminum and then onto a take-up spool. The aluminum was melted in an alumina crucible having

dimensions of about 24.1 cm x 31.3 cm x 31.8 cm (9.5"x12.5"x12.5") (commercially available from Vesuvius McDaniel of Beaver Falls, PA). The temperature of the molten aluminum was approximately 720°C. An alloy of 95% niobium and 5% molybdenum was fashioned into a cylinder having dimensions of about 12.7 cm (5") long x 2.5 cm (1") diameter. The cylinder was used as an ultrasonic horn actuator by tuning to the desired vibration (i.e., tuned by altering the length), to a vibration frequency of about 20.0-20.4 kHz. The amplitude of the actuator was greater than 0.002 cm (0.0008"). The actuator was connected to a titanium waveguide which, in turn, was connected to the ultrasonic transducer. The fibers were infiltrated with matrix material to form wires of relatively uniform cross-section and diameter. Wires made by this process had diameters of about 0.13 cm (0.05").

5

10

15

20

25

30

The volume percent of fiber was estimated from a photomicrograph of a cross section (at 200x magnification) to be about 40 volume %.

The tensile strength of the wire was 1.03 - 1.31 GPa (150-190 ksi).

The elongation at room temperature was approximately 0.7-0.8%. Elongation was measured during the tensile test by an extensometer.

Example 3-Composite Metal Matrix Materials Using an Al/Cu Alloy Matrix

This example was carried out exactly as described in Example 1, except that instead of using pure aluminum, an alloy containing aluminum and 2% by weight copper was used. The alloy contained less than about 0.02% by weight iron, and less than about 0.05% by weight total impurities. The yield strength of this alloy ranged from 41.4 - 103.4 MPa (6-15 ksi). The alloy was heat treated according to the following schedule:

520°C for 16 hours followed by a water quench (water temperature ranging from 60 -100°C); and

immediately placed into an oven at 190°C and held for 5 days.

The processing proceeded as described for Example 1 to produce rectangular pieces to make coupons suitable for tensile testing except that the metal was heated to 710°C and the mold (with the fibers in it) was heated to greater than 660°C.

The composite contained 60 volume % of fiber. The longitudinal strength ranged from 1.38 - 1.86 GPa (200 - 270 ksi) (with the average of 10 measurements of 1.52 GPa (220 ksi)) and the transverse strength ranged from 239 - 328 MPa (35 - 48 ksi) (with an average of 10 measurements of 262 MPa (38 ksi)).

5

10

Equivalents

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

5

10

25

What is claimed is:

- 1. A composite material which comprises at least one fiber of a polycrystalline α -Al₂O₃ having a tensile strength of at least about 2.8 GPa contained within a matrix of elemental aluminum that is substantially free of material phases or domains capable of enhancing brittleness in the fiber or matrix.
- 2. A composite material which comprises at least one fiber of a polycrystalline α-Al₂O₃ having a tensile strength of at least about 2.8 GPa contained within a matrix, the matrix comprising an alloy of elemental aluminum and up to about 2% copper and characterized in that it is substantially free of material phases or domains capable of enhancing brittleness in the fiber or matrix.
- 3. A composite material as in claim 1 or 2 wherein said at least one fiber is substantially continuous.
 - 4. A composite material as in claim 1 or 2 which comprises between about 30-70% polycrystalline α -Al₂O₃ fibers.
- A composite material as in claim 1 or 2 which comprises between about 40-60% polycrystalline α-Al₂O₃ fibers.
 - 6. A composite material as in claim 1 or 2 wherein said elemental aluminum matrix contains less than about 0.03% iron
 - 7. A composite material as in claim 1 or 2 wherein said elemental aluminum matrix contains less than about 0.01% iron.
- 8. A composite material as in claim 2 wherein said matrix has a yield strength of less than about 90 MPa.

9. A wire which comprises a plurality of substantially continuous polycrystalline α-Al₂O₃ fibers within a matrix, the matrix selected from the group consisting of substantially pure elemental aluminum and an alloy of elemental aluminum and up to about 2% copper.

5

20

25

- 10. A wire as in claim 9 wherein said at least one fiber is substantially continuous.
- 11. An overhead high voltage power transmission cable which comprises a plurality of aluminum matrix composite wires each of which comprises a plurality of substantially continuous polycrystalline α-Al₂O₃ fibers within a matrix, the matrix selected from the group consisting of substantially pure elemental aluminum and an alloy of elemental aluminum and up to about 2% copper.
- 15
 12. An overhead high voltage power transmission cable as in claim 11 which further includes at least one conductive jacket comprising a plurality of conductive aluminum or aluminum alloy wires.
 - 13. The article of claim 9 or 11 wherein said aluminum matrix composite wires comprise between about 30-70% polycrystalline α -Al₂O₃ fibers.
 - 14. The article of claim 9 or 11 wherein said aluminum matrix composite wires comprise between about 40-60% polycrystalline α -Al₂O₃ fibers.
 - 15. The article of claim 9 or 11wherein the matrix of said aluminum matrix composite wires contains less than about 0.03% iron.
 - 16. The article of claim 9 or 11 wherein the matrix of said aluminum matrix composite wires comprises substantially pure elemental aluminum having a yield strength of less than about 20 MPa.

17. The article of claim 9 or 11 wherein the matrix of said aluminum matrix composite wires comprises an alloy of elemental aluminum and up to about 2% copper, and further wherein the matrix has a yield strength of less than about 90 MPa.

- 18. The article of claim 9 or 11 wherein said polycrystalline α -Al₂O₃ fibers have a longitudinal tensile strength of at least about 2.8 GPa.
- 19. The article of claim 12 wherein said conductive aluminum wires of the conductive jacket comprise a material selected from the group consisting of 1350 Al and 6201 Al.

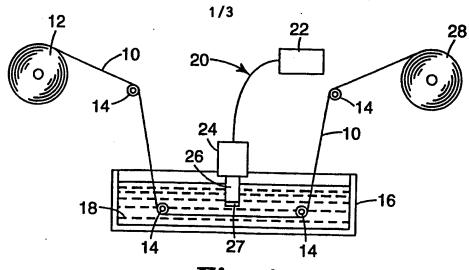


Fig. 1

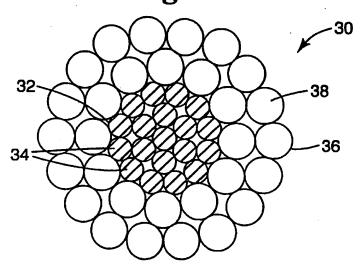
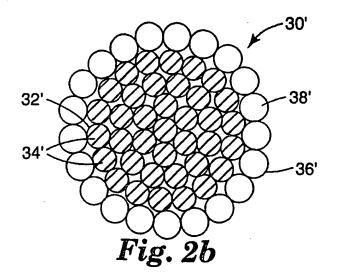
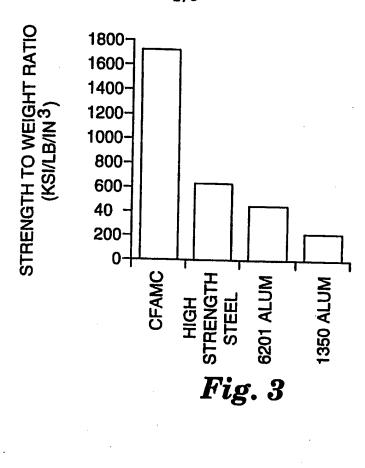
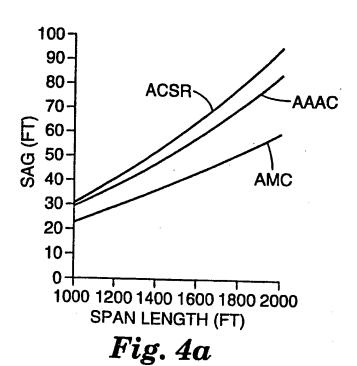
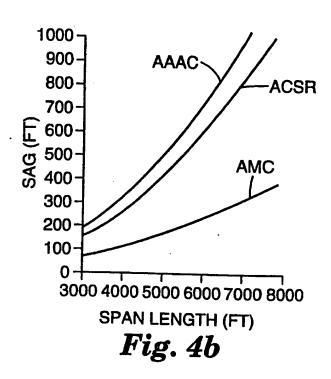


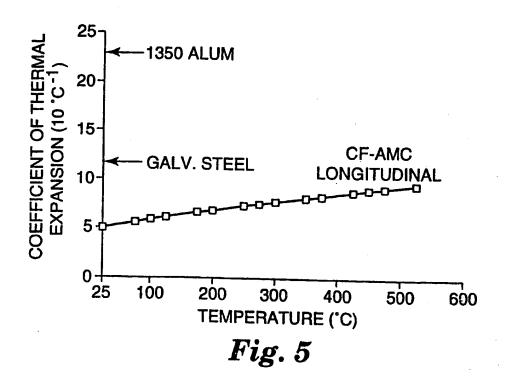
Fig. 2a











INTERNATIONAL SEARCH REPORT

Inter and Application No PCT/US 96/07286

A. CLAS	SIFICATION OF SUBJECT MATTER		
IPC 6	C22C1/09 H01B1/02		
According	to International Patent Classification (IPC) or to both national cl	assification and IPC	
	DS SEARCHED	•	
Minimum IPC 6	documentation searched (classification system followed by classific C22C H01B	cation symbols)	
Document	ation searched other than minimum documentation to the extent th	at such documents are included in the	fields searched
Electronic	data base consulted during the international search (name of data	tope and sub-	
	the state of the s	oase and, where practical, search term	s used)
		· 	
	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	: relevant passages	Relevant to claim No.
X	US,A,4 053 011 (RIEWALD PAUL GO	RDON ET AL)	1,3-5
Y	see column 1, line 39 - line 53		9-11,
A	see column 2, line 40 - line 42		13-16,18 2,6,7,9,
	see column 3, line 60 - line 63		11
Υ .	DATABASE WPI Section Ch, Week 9123 Derwent Publications Ltd., Londo Class L03, AN 91-167842 XP002011454 & JP,A,03 101 011 (FURUKAWA ELEC 25 April 1991 see abstract	•	9-11, 13-16,18
		-/	
Y Furt	her documents are listed in the continuation of box C.	V	
	tegories of cited documents:	X Patent family members are	listed in annex.
		"T" later document published after t	he international filing date
COUNTS	ent defining the general state of the art which is not ered to be of particular relevance	or priority date and not in conficient to understand the principle invention	lict with the application but e or theory underlying the
"E" earlier i	document but published on or after the international date	"X" document of particular relevance	e; the claimed invention
"L" docume	ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another	cannot be considered novel or o involve an inventive step when	annot be considered to
citation	n or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or	"Y" document of particular relevano cannot be considered to involve	e; the claimed invention
outer r	neans	ments, such combination being	or more other such does-
later th	ent published prior to the international filing date but aan the priority date claimed	in the art. "&" document member of the same p	
Date of the	actual completion of the international search	Date of mailing of the internation	
27	2 August 1996	2 7. gg	
Name and n	nailing address of the ISA	Authorized officer	
	European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk		
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ashley, G	

Form PCT/ISA/218 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter. 121 Application No PCT/US 96/97286

Category *	tion) DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages	
	and appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 95, no. 004 & JP,A,07 105761 (TOKYO ELECTRIC POWER CO INC:THE;OTHERS: 01), 21 April 1995, see abstract	11
A	US,A,4 757 790 (USHIO HIDEAKI ET AL) 19 July 1988	
	·	

INTERNATIONAL SEARCH REPORT

information on patent family members

Inte onal Application No PCT/US 96/07286

			101/00 00/01	
Patent document cited in search report	Publication date		family ber(s)	Publication date
US-A-4053011	11-10-77	US-A-	4012204	15-03-77
US-A-4757790	19-07-88	JP-C- JP-B- JP-A- CA-A- DE-A- GB-A,B	1648159 3008867 62064467 1287240 3631096 2183785	13-03-92 07-02-91 23-03-87 06-08-91 26-03-87 10-06-87

Form PCT/ISA/210 (patent family annex) (July 1992)